Degradation of Aqueous Rhodamine B By Catalysis Zone Extension of Modified Dyes Sensitized Solar Cell.

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Abstract

A modified dyes sensitized solar cell (DSSC) having catalysis zone have been successfully developed. The modified DSSC comprise of DSSC zone, employing a rhodamine B as the sensitizer, and catalysis zone, a simple an extension of the TiO_2 nanotube film support which was not covered by dyes. The TiO_2 nanotube was prepared by rapid breakdown anodization (RBA) method followed by heating treatment of obtained amorphous TiO_2 nanotube, and charactetization by UV-Vis DRS, XRD, and SEM. Briefly, the obtained TiO_2 has a bundling nanotube morphology, crystalline phase and typical band gap of anatase and rutile mixture (depend on heating temperature). The catalysis zone was tested to treat a water sample containing organic chemical (rhodamine B), as a pollutant model. Test results indicated that the catalysis zone enable to eliminate of rhodamine in the treated water, due to subsequent process starting by generation of super oxide ($.O_2^-$) in adjacent TiO_2 surface, leading to hydroxyl radical which in turn degrade the rhodamine B. This result indicate that the injected electron from dyes, upon visible light absorption, to conduction band of TiO_2 in DSSC zone was successfully migrated to TiO_2 surface in catalysis zone.

Keywords : DSSC-Catalysis, TiO_2 nanotube, rapid breakdown anodization, rhodamine B, mixed phase anatase rutile.

1. Introduction

Photocatalyst involving TiO_2 semiconductor has been studied extensively toward its ability to degrade toxic organic in water and air as well [1]. However, the critical obstacle still persist, in which that the TiO_2 semiconductor can only be activated by UV light, due to its wide band gap energy (3.00 to 3.20 eV). Thus any developed photo-catalytic system was not able to fully utilized abundance sunlight available. Many efforts have been conducted to shift the band gap energy toward visible light, by doping the TiO_2 with transitional metals and non metallic elements such is nitrogen and others [2,3]. At the moment, no one can predict the proper dopant fraction that resulting intended band gap shift without degrading the photo catalytic performance.

On the other hand, research in dyes sensitized solar cell (DSSC) has showed quite successfully in converting solar light to electricity [4,5]. This mean in the DSSC system, the absorbed visible light successfully converted to the injected electrons in the conduction band of semiconductor (TiO_2). In this sense we interested to explore the injected electrons in the TiO_2 matrixes (in the DSSC system) is not only for the electricity generation but will be diverted to the invented catalysis zone, in which there is a dyes uncovered zone of TiO_2 part, for a reduction and oxidation reaction with chemicals in adjacent surface.

Recently, Qin et al in 2011 [6,7] developed a modified dyes sensitized solar cell (DSSC) having catalysis zone extension. This modified DSSC is basically a Gratzell type solar cell, in which the TiO_2 part has an extension to the one that was not covered by the dyes (Figure 1). A zone in which the TiO_2 was being covered by dyes, sandwiched with electrolyte and transparent Pt film counter electrode. This DSSC zone has function to crop visible light and injected electron to TiO_2 conduction band. While a zone where the extended TiO_2 is not being covered by dyes will be immersed to the reaction medium (e.g. water containing toxic chemicals), has a function to delivered electron to the interface, designed as catalysis zone.

Qin et al developed such system, employing porous TiO_2 and ruthenium based organic dyes, and reported that the system was able to degrade 4-Chlorophenol in water [6] and converting CO_2 to formic acid, formaldehyde, and methanol [7]. Based on this Qin et al system, we developed a modified DSSC-catalysis hybrid system employing simple rhodamine B as sensitizing dyes and self prepared TiO_2 nanotube powder as the semiconductor support and catalyst zone as well. The preparation and characterization of TiO_2 nanotube (TiO_2-NT)powder, the assembly of modified DSSC and its catalytic ability of the catalysis zone to degrade

organic chemicals will be presented and discussed.

2. Experiment

Material and Chemicals. A plain glass plate (75 mm x 25 mm) as electrode, titanium plate (45 mm x 10 mm) with the thickness of 0.2 mm, Pt Foil and plate, 0.1 M $HClO_4$ (pa) from Merck , Ethanol (technical), Acetone (technical), Isopropyl Alcohol (technical), distilled water, Potassium iodide (KI), Iodine (I_2), Dragon Fruit Extract, Rhodamine B, Acetic Acid 0.2 %, Triton X – 100 from Merck, $SnCl_2.2H_2O$ from Merck, H_2PtCl_6 from Merck, abrasive paper CC1000 and CC1500

Preparation of TiO_2 Nanotube. TiO_2 nanotubes were synthesized by anodization of titanium plate through RBA method at 15 V in 0.15 M $HClO_4$ [8]. The products were washed at 400°C and 500°C for 2 hours and 3 hours. TiO_2 nanotubes powder were characterized by UV-Vis Spectrophotometer DRS (Shimadzu 2550), Field Emission Scanning Electron Microscope (FESEM), X-ray Spectrometer Diffraction (Miniflex).

Preparation of Modified DSSC System.

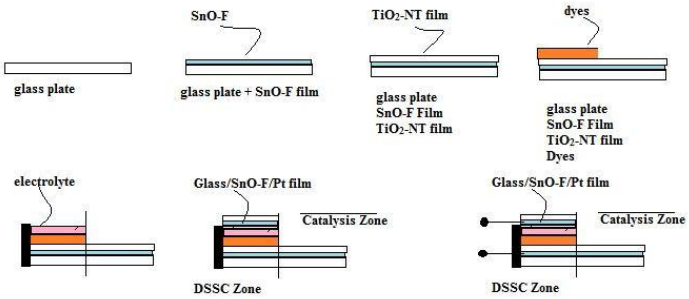
Cathode: Fluor Tin Oxide (FTO) glass was sonicated in ethanol for 2 hours and then coating of Pt film was conducted by dropping of H_2PtCl_6-2propanol solution on the conductive surface of the glass, followed by heating treatment at 450°C for 10 minutes.

Anode : FTO glass was sonicated in ethanol for 2 hours. TiO_2 paste was prepared using TiO_2 nanotubes powder, CH_3COOH 0.2% and Triton-X and was conducted according to Doctor Blade method. The TiO_2 coated FTO then were dried in air at 120°C and calcined at 450°C for an hour.

DSSC-Catalysis Hybrid System Assembly. Half of TiO_2 film that has been deposited on FTO glass was immersed in rhodamine B for 5 minutes (as synthetic dye system). After absorption, the TiO_2 film-dye was washed by ethanol and dried in ambient temperature for a few minutes. To prevent direct contact between TiO_2 film-dye with a counter electrode (Pt), the TiO_2 film-dye and Pt-film counter electrode were separated by parafilm (127 µm thick) and sealed by heating in sandwich form as shown in Figure 1.A.

Degradation Experiment Using DSSC-Catalysis Hybrid System. A 400 Watt HPS lamp (λ_{max} = 500-600 nm) was used as a source of visible light , which was placed at a distance of 20 cm from the surface of TiO_2 films in DSSC zone. Irradiation was exposed for 25-30 minutes, while the chamber filled with treated water containing certain amount of dissolved rhodamine B. The remaining concentration of rhodamine B was measured by UV-Vis spectrometer at intervals of 5 minutes.

[A]



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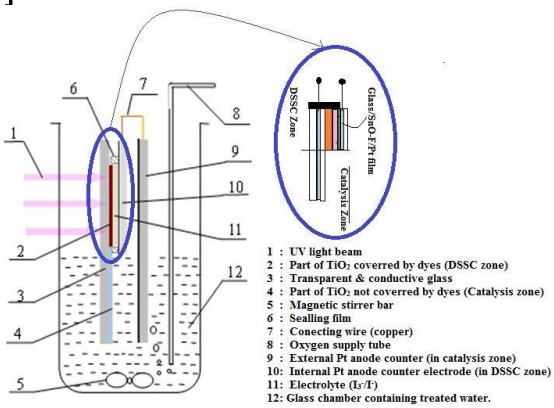

Figure 1. Schematic of Modified DSSC-Catalysis Hybrid Reactor System (above) and Chronological Assembly of Modified DSSC (bottom) (adapted from Qin et al., 2011[6&7])

3. Result and Discussion

Characterization of TiO_2 Nanotube Powder.

X-Ray diffraction pattern measurements are showed in Figure 3.

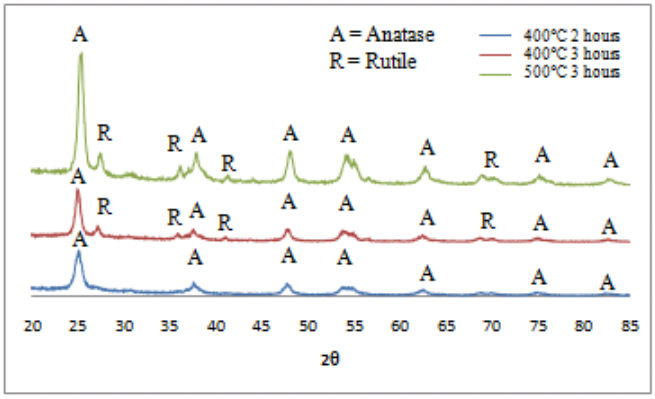

Figure 3. Diffractogram of TiO_2 Nanotube After Calcination

Determination of rutile phase in the samples has been done by using equation 6 and the result can be seen in table 1.

$$X_r = \frac{I_r}{0.886I_a + I_r} \times 100\% \qquad (6)$$

Where :

X_r : Rutile content in the sample (%)

I_r : Highest Intensity of rutile phase

I_a : Highest Intensity of anatase phase

Table 1. Anatase and Rutile Content in Calcined Samples

Calcined TiO_2	Rutile (%)	Anatase (%)
500°C 3 hours	17,08	82,92
400°C 3 hours	7,12	92,88
400°C 2 hours	0,00	100

Optical band gap of samples can be determined by using UV VIS DRS. In this work, the band gap energy determined using Tauc Plot between energy (E) and reflectance factor square ($F(R)^2$) derived from Kubelka-Munk function

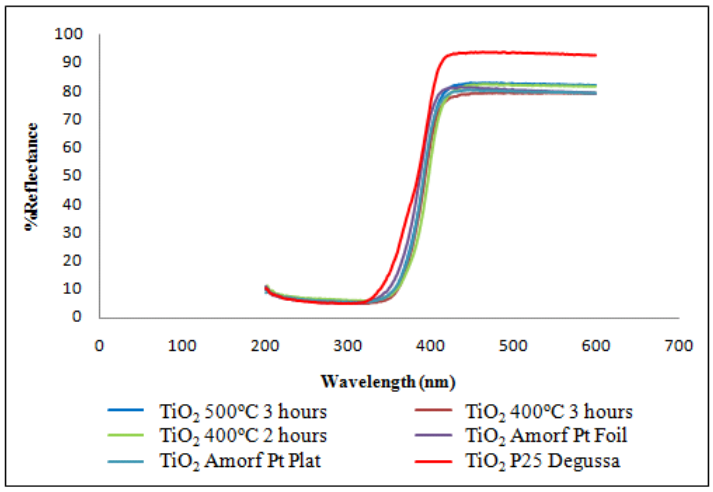

Figure 4. Wavelength vs %Reflectance of Samples

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R} \qquad (7)$$

$$F(R)^2 = \left(\frac{A}{S}\right)^2 hv - \left(\frac{A}{S}\right)^2 Eg \qquad (8)$$

F(R) is Kubelka-Munk function, R is the intensities ratio of the reflectance in sample and in standard, K is adsorption coefficient, S is scattering factor, A is proportional constant, and Eg is optical band gap energy. The result of band gap determination can be seen in Table 2.

Table 2. Optical Band Gap of TiO_2 Nanotubes

Samples	Band Gap (eV)
500°C 3 hour	3.34
400°C 3 hour	3.36
400°C 2 hour	3.38
Amorf	3.42
Degussa P25	3.45

FESEM characterization. The morphology of TiO_2 nanotubes and elemental examination of the prepared TiO_2 has conducted by FESEM-EDX characterization. Figure 5 describes the result of FESEM and EDX respectively. The image of TiO_2 nanotubes bundles can be seen in Figure 5, in which the outer diameters of bundles were about 71.4 nm - 83.3 nm, the length was approximately 10 µm and only 2 elements (Ti and O) peak signal appear ensuring purity of TiO_2-NT prepared.

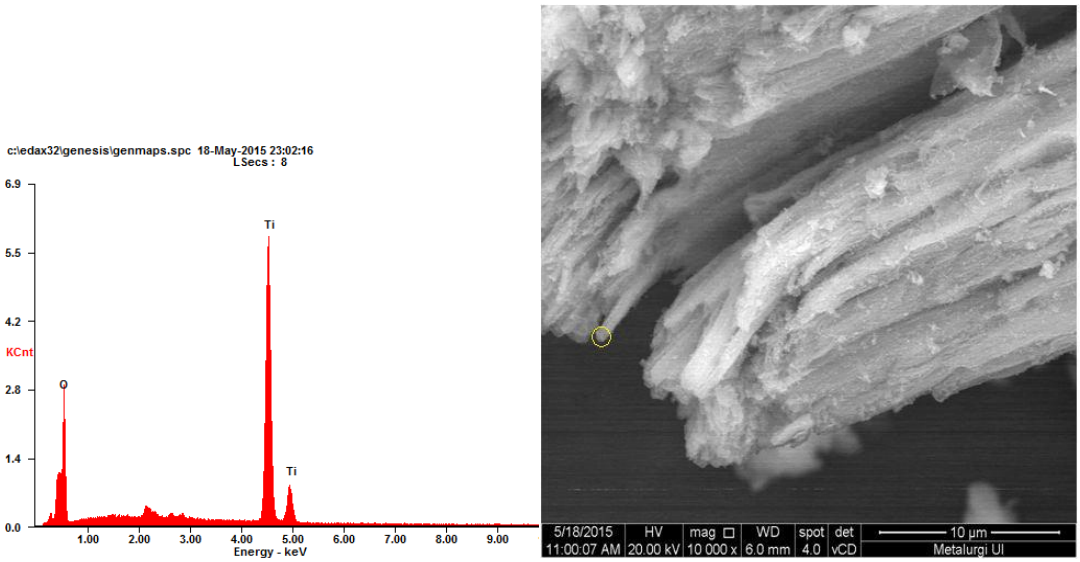

Figure 5. FESEM picture shows a morphology of TiO_2 Nanotube and its EDX spectrum

The influence of anatase-rutile crystalline phase ratio.

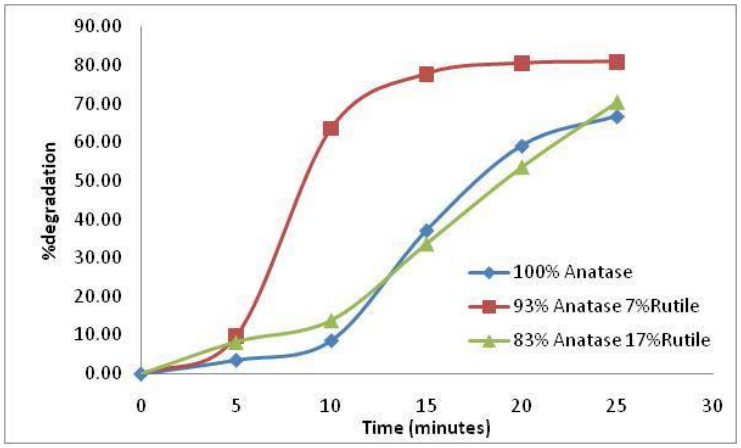

Figure 6. Degradation Activity Testing Based on Mixed Anatase-Rutile Crystalline Phase

As shown in Fig. 6, when relatively pure anatase was being applied the degradation performance was lower than that of when a mixed of anatase-rutile (93:7) was being applied. However when the rutile fraction was increased no more improvement of degradation performed was observed. This mean that only a proper composition that will lead to the improvement of the degradation performance.

When electron and hole formed, in a proper composition of anatase-rutile ratio, electron willmigrate from the higher energy to the lower one. Based on Scanlon et al in 2013, the valenced band energy of anatase is 2,81 eV and rutile 3,03 eV while the conduction band energy of anatase and rutile are -0,39 eV and 0 eV respectively. From the data, it is known that after electron injected into TiO_2 conduction band, potential difference between fraction of anatase (-0.39eV) and rutile (0.00 eV) will create additional driving force for the migration of electrons to the catalysis zone. This will provide more active electron in the catalysis zone surface, hence more superoxides were formed.

4. Conclusions

Modified DSSC, a DSSC-Catalysis hybrid system has been successfully developed and the catalysis zone was successfully able to degrade rhodamine B in water. The ratio of DSSC zone and catalysis zone influence the catalysis performance, in which in this work, the best performance was found when the ratio was 1 : 2. In addition the ratio of anatase to rutile fraction was also influence the catalysis performance, so far the ratio of anatase to rutile at 93:7 showed the best one.

Acknowledgement

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